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GHGT-12

Performance evaluation of carbon dioxide sequestration in oil shale fly ashes

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Abstract

This work investigated the performance of oil shale fly ashes (OSFA) as feedstock for CO₂ mineral carbonation using an ammonium salts based pH swing process. A CO₂ uptake of 156 kg CO₂/t ash was obtained for the OSFA from cyclones. This CO₂ uptake was similar to that previously obtained using a direct mineral carbonation process with less favorable process scale up conditions. Among pulverised fuel ashes, OSFA samples collected from the electrostatic precipitation tend to present lower CO₂ uptake compared to the OSFA sample obtained from the cyclones. OSFA from circulating fluidised beds were found to be less attractive for CO₂ sequestration process with ammonium salts.

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Keywords: CCS, mineral carbonation, oil shale fly ashes, CO₂ sequestration.

1. Introduction

Carbon Dioxide Capture and Storage (CCS) is widely regarded as one of the main strategies for reducing anthropogenic CO₂ emissions. Once CO₂ has been captured from large stationary sources, there are a number of methods of storage- for example, in geological formations. There are also a number of industrial uses for CO₂, including enhanced oil recovery or in mineralisation reactions to produce useful carbonate materials.

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Mineral sequestration mimics the natural weathering of silicate rocks, where CO_2 reacts with the cations (e.g. Ca^{2+} , Mg^{2+}) present in the silicates producing carbonates, which permanently sequester CO_2 [1].

Despite the fact of being energetically favoured, mineral carbonation reactions are kinetically limited. In particular, the silicates dissolution rate is much slower than the corresponding carbonation rate. Recent studies have focused on enhancing the extraction of the reactive cations from silicate rocks by employing leaching agents, such as ammonium salts [2-5] that can be recycled. This mineralization process has been applied to silicate rocks, steel slags and concrete waste. Inorganic wastes present some advantage over fresh rocks, since they do not need to be mined, and often are co-located close to the CO_2 emitter and do not require extensive comminution [3,5-9].

The objective of this work is to study the potential use of oil shale ashes for mineral carbonation. Oil shale reserves are widely distributed around the world ($2900 \cdot 10^9$ barrels of oil equivalent), with Estonia having one of the world largest deposits of commercial significance [10]. Generally, oil shale ash contains about 40-50% of total CaO , which make them an attractive feedstock for mineral carbonation [7].

2. Method

Four oil shale fly ash (OSFA) samples from Estonian power plants were evaluated for their potential use in indirect mineral carbonation for CO_2 sequestration. The OSFA samples contain CaO content between 35 and 51 wt% as shown in Figure 1 and include: Sample 1 collected from a pulverized firing boiler (cyclone ash); Sample 2 from the 1st field of electrostatic precipitator (pulverized firing); Sample 3, collected in the DeSOx plant (pulverized firing); and finally, Sample 4 obtained from the 1st field of electrostatic precipitator of a circulating fluidized bed combustor.

Table 1 presents the specific surface area and particle size distribution (D90) for the study samples. From the point of view of mineral carbonation, sample 2 and 3 seem better feedstock compared to sample 1 and 4, because of their larger surface area and smaller particles size.

Table 1. Specific surface area and particle size distribution (D90) for study samples.

Sample	CaO, wt%	Specific surface area, m^2/g	D90 particle size, μm
1	47.41	1.70	97.93
2	51.11	4.15	35.60
3	34.84	4.22	35.24
4	39.48	3.27	79.41

Dissolution studies were performed at 90°C , solid to liquid ratio of 50g/L, stirring rate of 800rpm and in the presence of excess NH_4HSO_4 (1.4M). Qualitative information on the reactions was obtained by FTIR analysis using standards, while quantitative analyses on abundance of metal leaching were performed by ICP-MS. The carbonation of the better dissolving shale ash was studied at 60°C in presence of stoichiometric amount of $(\text{NH}_4)_2\text{CO}_3$. The carbonation yield was evaluated by FTIR and quantified by TGA-MS.

3. Results and Discussion

Figure 1 presents the dissolution of the different oil shale fly ash samples using NH_4HSO_4 at 90°C . The results indicate that OSFA samples present comparable carbonation efficiency to steel slag using the ammonium base process. Moreover, the cyclone ash (Sample 1) and 1st field of electrostatic precipitator ash from the pulverized firing boiler (Sample 2) were the most reactive samples in terms of CO_2 carbonated.

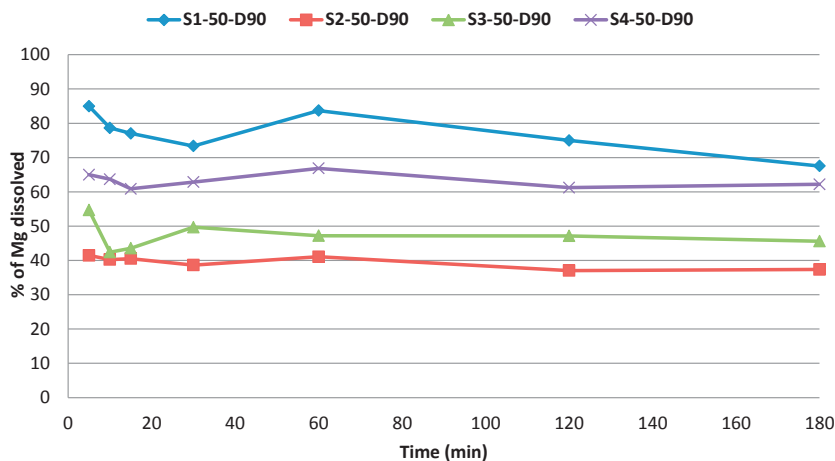


Figure 1 Dissolution of Mg for different OSFA Samples. S1-50-D90 stands for: S1 (Sample 1); 50 (solid to liquid ratio of 50g/L); D90 (dissolution temperature, 90°C).

XRD analysis of Sample 1 (Figure 2) and Sample 2 (Figure 3) were carried out in an attempt to ascertain why dissolution results produced from Sample 2 were significantly lower compared to sample 1. It was found that the composition, particularly of the calcium components present, varied significantly between Sample 1 and 2, where Sample 2 showed a larger presence of CaSO_4 and SiO_2 in particular. The high proportion of calcium already present in the sample as calcium sulphate is likely to be responsible for the poor performance of Sample 2 during dissolution; since this form of calcium cannot be detected by ICP-MS (CaSO_4 is insoluble in water). The high silica content also contribute as silicates may be responsible for blocking pores on the surface of the oil shale particles and preventing diffusion and replacement of protons with calcium into the particle. In fact, previous work shows that silica is very difficult to dissolve [11]. These factors suggest that the reaction mechanism and kinetics may be controlled by diffusion on the outer layer of the OSFA particle. Since Sample 1 is richer in free CaO and also present less SiO_2 , its dissolution efficiency was found higher than that using Sample 2.

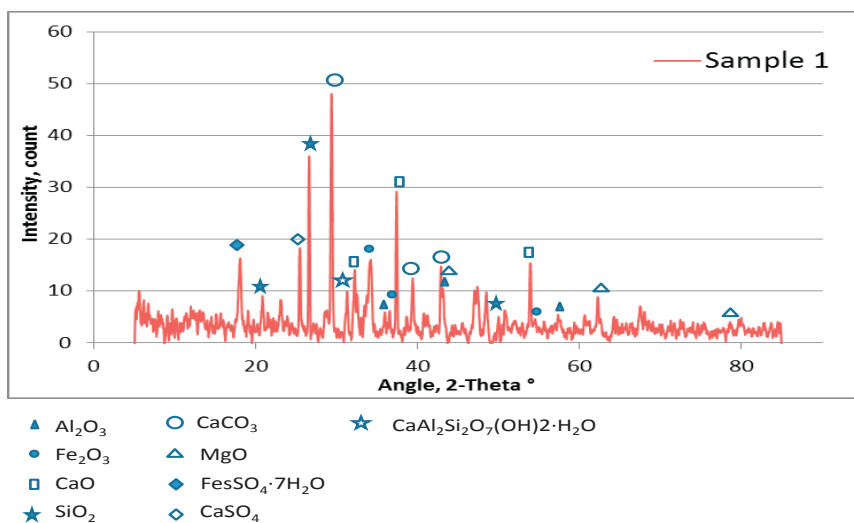


Figure 2 - XRD analysis for sample 1.

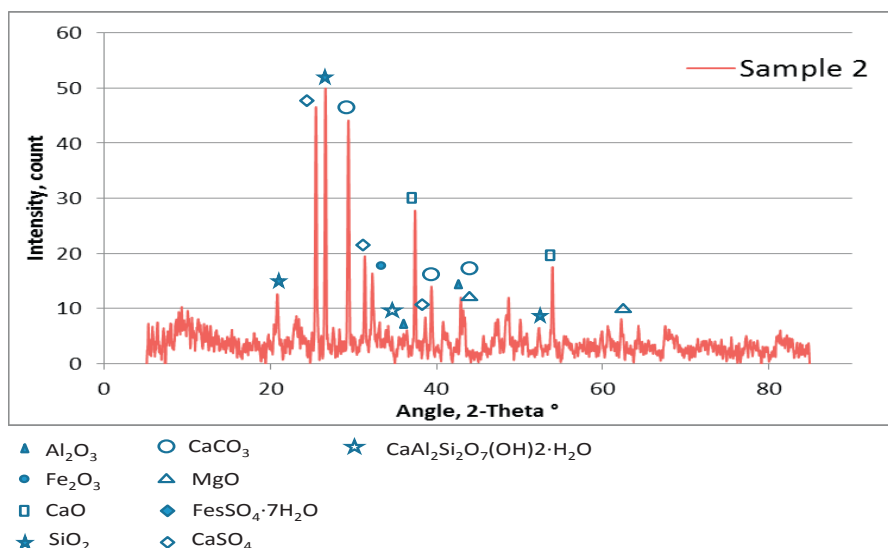


Figure 3 - XRD analysis for sample 2.

Table 2 reports the efficiency of the carbonation stage using the four different materials. Pulverized Oil Shale Fly Ash is characterized by a theoretical CO_2 capacity of 350-500 Kg CO_2/t , which is based on CaO content [12]. Despite this, the direct carbonation of both pulverized fuel oil ash and ash from circulating fluidized bed combustor achieved much lower carbonation efficiency [13]. An uptake of 155 kg CO_2/t ash was achieved by diluting the ash process water to 90% (solid liquid ration of 10g/L) or by using a 6 month ageing pre-treatment to increase the porosity of fly ash. An even lower CO_2 uptake (135 kg CO_2/t ash) was obtained when oil shale ash combusted in a circulating fluidised bed were used. To compare the CO_2 uptake obtained in this work, the dissolution and carbonation efficiency in terms of Ca dissolved and carbonated should be considered.

Sample 1 that is a pulverized fuel oil shale ash was the material more prone to dissolution and carbonation among the tested samples. Its CO_2 uptake was of 156 kg CO_2/t ash (1t sample 1 contains 474kg CaO, 80% of which is dissolved and 52% (of the 80%) is carbonated, giving a CO_2 uptake of 156kg and considering that each t of CaO can uptake 78.6% CO_2) resulting in an overall efficiency of 42% under the studied conditions. This was comparable to the CO_2 uptake obtained from the direct carbonation (ambient temperature and pressure) [13]. Confirming the trend found by Uibu and Kuusik [13], the fuel oil shale ash from the circulating fluidized bed achieved a lower CO_2 uptake, with 100 kg CO_2/t ash. Further work on the optimization of the dissolution and carbonation steps will be presented.

Table 2. Carbonation efficiency of samples.

Sample	Carbonation stage efficiency, %	CO_2 uptake, kg CO_2/t ash
1	52	156
2	35.5	56
3	45	63
4	48	100

4. Conclusions

The first conclusion that can be drawn is that oil shale fly ash (OSFA) can be used as a successful feedstock for carbon capture and storage by mineralisation (CCSM) using the ammonium-based process.

CO₂ uptake of sample 1 was of 156 kg CO₂/t ash resulting similar to CO₂ uptake previously obtained using different mineral carbonation processes after 6 months ash aging pre-treatment.

Among pulverised fuel ashes, OSFA particles from the electrostatic precipitation (Sample 2) tend to be less efficient compared to the particles separated by the cyclons (Sample 1). The calcium compounds within the particle have a large effect on efficiency. Sample 1, which has high levels of free CaO was found to present a higher carbonation efficiency compared to Sample 2 that contained high levels of calcium sulphate. In addition, Sample 2 was found to have high levels of silica, which is dissolution-resistant.

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